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PRODUCTION OF CERAMIC PIGMENTS BASED ON NATURAL WOLLASTONITE USING THE GEL METHOD

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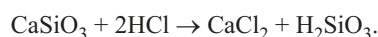
The authors consider the possibility of producing ceramic pigments based on natural wollastonite using the gel method, which contributes to the formation of an amorphous structure in wollastonite under the effect of hydrochloric acid. The chromophores are soluble salts containing Fe^{3+} , Ni^{2+} , Cr^{3+} , Cu^{2+} , and Co^{2+} ions. The wollastonite structure is restored under firing; the color characteristics of pigments after the gel-formation stage improve. The use of the gel method does not require a cardinal modification of the technological scheme and equipment but facilitates a significant improvement of the color properties of pigments and paints.

A disadvantage of using natural minerals with a crystalline structure as a basis for ceramic pigments is their limited capacity for assimilating colorant ions.

To increase the ionic capacity of natural minerals, it is necessary to use nontraditional methods for ceramic pigment production. There are new methods including self-propagating high-temperature synthesis, synthesis using mechanochemistry, or the gel method used to produce ceramic pigments from chemically pure raw materials (RF patent No. 2120918) [1, 2].

The sol-gel method was first used in the production of ceramics 50 years ago; later, silica gel was investigated [3]. The advantages of the sol-gel technology include a high chemical homogeneity of multicomponent systems (at the molecular level), a high surface energy of gels and powders, which brings down the sintering temperature, the possibility of getting products in the form of fibers, powders, films, microspheres of high purity and homogeneity, the possibility of a direct transition from the amorphous state to the crystalline state without introducing mineralizing additives, etc. At present sol-gel technology is a progressive and promising method for producing materials.

The use of the sol-gel method in our study is based on the capacity of natural wollastonite mineral to form an amorphous structure under the effect of hydrochloric acid. When HCl is added to wollastonite, gel formation takes place, since silicic acid and calcium chloride are formed:



At this stage the dispersion of the batch and homogenizing of the components at the molecular level take place. It is assumed that a structure in the gel form is capable of assimilating a greater quantity of colorant ions than in its crystalline state. In subsequent firing the crystalline structure of wollastonite is restored.

Pigments were obtained using the following method. Natural wollastonite was subjected to dry milling in a ball mill to a grain size not more than 0.2 mm. In our study we used wollastonite from the Slyudyanskoe deposit, which is unique due to its low content of colorant impurities. The mineral content is 95 – 97% (here and elsewhere, wt.%). The chemical composition of concentrated Slyudyanskoe wollastonite is as follows (%): 46.98 SiO_2 , 0.10 Al_2O_3 , 0.04 Fe_2O_3 , 49.42 CaO , 1.22 MgO , 0.13 P_2O_5 , and 2.11 calcination loss.

Wollastonite was mixed with water-soluble salts of the elements of subgroup 3-d in an amount of 5 – 20% (converted to oxide); then a small quantity of concentrated hydrochloric acid was added into the mixture for the specified reaction to take place. The resulting gel was dried and fired at a temperature of 1000 – 1200°C. The resulting cake was milled to a residue not more than 0.2% on a No. 0063 sieve.

Composition of Pigments (Converted to Oxide) Based on (80 – 95%) Wollastonite

Pigment	Content %
V-1 – V-4	5 – 20 CoO
V-5 – V-8	5 – 20 CuO
V-9 – V-12	5 – 20 Fe_2O_3
V-13 – V-16	5 – 20 NiO
V-17 – V-20	5 – 20 Cr_2O_3

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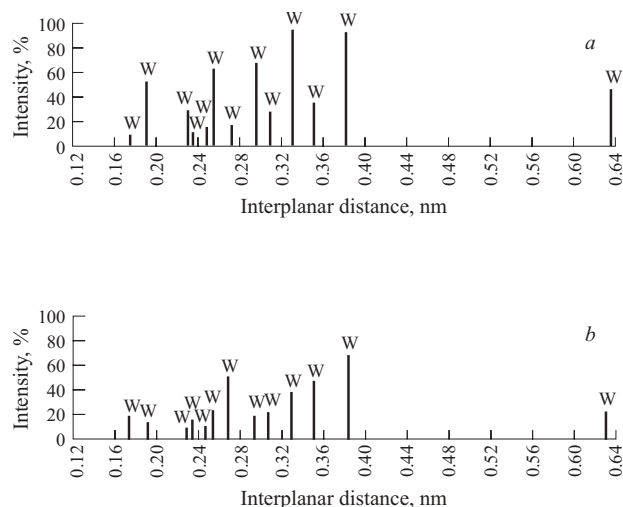


Fig. 1. X-ray diffraction diagrams of blank tests of wollastonite having passed the gel formation stage (*a*) and not subjected to gel formation (*b*). Firing temperature 1100°C: W) wollastonite.

Visual inspection of the pigments showed their diverse color shades (Table 1). Raising the firing temperature to 1200°C does not give a positive result with respect to getting bright coloring. Furthermore, most pigments at this temperature pass into a melted state. The optimum temperature should be regarded as 1100°C, at which the pigments have the maximally bright color and do not melt.

The comparison of the colors of pigments that were or were not subjected to gel formation suggests that in the first case the pigments have better chromophore properties.

The synthesized pigments were tested as underglaze ceramic paints. They were deposited on prefired ceramic articles and coated by a low-melting lead-free glaze. Firing was performed at a temperature of 1050°C. After firing, the paints had bright shades (Table 1) and were resistant to the effect of high temperatures and melted glaze.

The x-ray phase analysis established that the wollastonite structure in pigments is restored even under firing at a temperature of 1000°C. The comparison of blank test diffraction patterns indicates that the gel formation stage increased the crystallinity of the wollastonite structure, which is expressed in an increased intensity of the main diffraction peaks

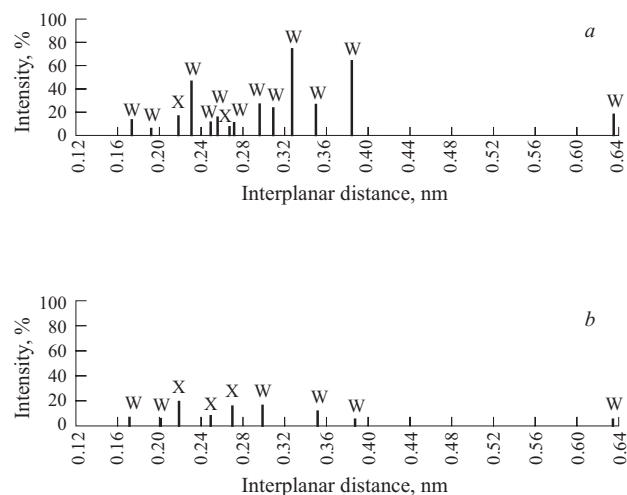


Fig. 2. X-ray diffraction diagrams of pigments V-17 – 5% Cr₂O₃ (*a*) and V-20 – 20% Cr₂O₃ (*b*). Firing temperature 1100°C: W) wollastonite; X) Cr₂O₃.

(Fig. 1). Furthermore, the ratio of intensities of x-ray maxima for the same crystalline planes is modified, which is due to a different morphology of wollastonite particles depending on its formation conditions.

Upon adding a small quantity of a chromophore (5%) the structure virtually does not change; however, Cr₂O₃ in the free form becomes registered in pigments with chromium, which is evidenced by the peaks on the diffraction patterns: $d = 0.267$ and 0.217 nm (Fig. 2). Upon adding 20% Cr₂O₃, the wollastonite structure gets destroyed and the peaks become very low. In pigments with iron a small quantity of Fe₂O₃ ($d = 0.252$ and 0.383 nm) is registered starting with the pigment content of 10%. In cobalt and nickel pigments small peaks typical of these oxides are observed with a 10% chromophore content: CoO ($d = 0.143$ and 0.244 nm) and NiO ($d = 0.241$ and 0.208 nm), which intensify with increasing chromophore content. The crystalline structure of wollastonite in this case is preserved.

The spectrophotometric analysis recorded spectral reflection curves using a SF-18 spectrophotometer, and chromaticity coordinates X , Y , and Z were calculated. Based on the color triangle, the wavelength and tone purity of the pigments were determined (Table 2). The analysis of these data shows that increasing the content of cobalt oxide in pigments

TABLE 1

Pigment	Color of pigments after firing at temperature of 1100°C	Color of paints after firing at 1050°C
V-1	Pale blue	Pale blue
V-3	Bright blue-purple	Blue-Purple
V-9	Pale coffee	Pale yellow-brown
V-12	Gray	Yellow-brown
V-13	Pale yellow-lettuce	
V-15	Yellow-green	
V-17	Pale green	Grassy-green
V-20	Grassy-green	

TABLE 2

Pigment	Chromaticity coordinates		Wavelength, nm	Color tone purity, %
	X	Y		
V-1	0.23	0.22	474	19
V-3	0.22	0.24	478	25
V-15	0.38	0.39	576	40
V-17	0.34	0.42	559	41
V-20	0.36	0.42	565	50

from 5 to 15% contributes to increasing the color saturation and modifying the color shade, which is manifested in a change of the dominant wavelength and tone purity.

Nickel oxide imparts a yellow-lettuce color tone to pigments; chromium oxide as well produces green tinting, but of a different shade. Pigments V-15 and V-17 differ in their wavelength and tone purity.

Thus, the use of the gel method for producing ceramic pigments is justified and promising, since it has a number of advantages. When finely milled material is treated with a colorant salt solution (without the gel-formation stage), the chromophore ions just get adsorbed on the surface of solid particles. The subsequent incorporation of the chromophore ions in the crystal lattice through diffusion to a great extent depends on the size of the initial mineral particles and on the ratio of the ionic radii of the interchanging ions and their charges. The gel method makes it possible to homogenize the mixture component at the molecular level. The need for long hours of joint milling of the components is eliminated. In the

course of the restoration of the crystal lattice of wollastonite, a larger quantity of colorant ions can be incorporated into the wollastonite structure.

The gel method can be recommended for the industrial production of ceramic pigments, as it does not require cardinal modifications of the process scheme and equipment but facilitates a significant improvement of the color properties of pigments and paints.

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